

THE EXALTATION FACTORS IN
CERTAIN MIXED ALLYL AROMATIC ETHERS

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA
August, 1956

ACKNOWLEDGMENTS

The author wishes to express his deep gratitude to Dr. George B. Butler whose teaching, direction, and encouragement contributed immeasurably to the completion of this work. The author is also indebted to his Supervisory Committee for their advice, suggestions, and encouragement. The author also wishes to thank Mr. Burton J. Otte and his staff for their cooperation in the matter of supplies and equipment, Mrs. Mary Joy Breton for typing the manuscript, and the many graduate students who indirectly, and probably unknowingly, contributed much to this work.

The author is also indebted to E. I. du Pont de Nemours and Company, Inc., for their support of this work by providing the author with a Teaching Fellowship for the academic year 1955-1956.

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CHAPTER I

INTRODUCTION

The molecular refractivity of a substance may be calculated by summation of empirically determined atomic and structural refractions, and may be determined experimentally from density and refractive index data using the familiar Lorentz-Lorenz equation. The positive deviation of the observed molecular refractivity from the calculated value is called an exaltation, which, as a rule, increases with increasing significance of the mesomeric effect (41, 112). It is well known that systems having conjugated multiple bonds and systems in which an aryl group is conjugated with a multiple bond exhibit exaltations of refraction. Since isoprene, styrene, and many other readily polymerizable substances exhibit exaltations of refraction, it was decided to prepare a series of allyl aromatic ethers and study the effect of exaltation on the rate of polymerization of these ethers.

The main objectives in this investigation were as follows:

- (1) To investigate the possible correlation of the exaltation of refraction with the rate of polymerization in homopolymerizations.

(2) To investigate the possible correlation of the exaltation of refraction with the rate of polymerization in copolymerizations.

(3) To prepare a series of allyl aromatic ethers and to determine their exaltations of refraction.

(4) To correlate the exaltation of refraction of these allyl aromatic ethers with their rates of polymerization in homopolymerizations and copolymerizations.

CHAPTER II

INVESTIGATION OF POSSIBLE CORRELATION OF THE EXALTATION OF REFRACTION WITH THE RATE OF POLYMERIZATION IN HOMOPOLYMERIZATIONS

Chitani (20) assumed that the exaltation of refraction was related to the rate of polymerization in vinyl compounds. Nakatsuka (83) attempted to prove the above assumption by using α -methylstyrene and β -methylstyrene as models; the latter has the higher exaltation and yields a dimer, while the former does not polymerize under similar conditions. The only other literature bearing on this work was a paper by Stempel et al. (106) who reported on the polymerization characteristics of several disubstituted α -methylstyrenes, and noted the differences existing in refractive indexes between these α -methylstyrenes and similarly substituted styrenes.

The following section deals first with the selection and use of the atomic and structural refractions in a few examples to illustrate the effect of structure and conjugation on the exaltation of refraction, and then an investigation of possible correlation of the exaltation of refraction with the rate of polymerization in homopolymerizations involving substituted styrenes.

A. Selection of Atomic and Structural Refractions

The widely-accepted atomic, group, and structural refraction values of Eisenlohr (28) listed by Weissberger (126) will be used in this work. Comparison with the more recent values of Vogel (118), using ethylbenzene as an example, is given in Table 1; EM_D is the exaltation of the molecular refraction, EZ_D is the exaltation of the specific refraction, and MR_D is the molecular refraction.

TABLE 1
EXALTATION OF ETHYLBENZENE

MR_D		EM_D	EZ_D
Calcd.	Obsd.		
35.543 ⁽²⁸⁾	35.752 ⁽¹¹³⁾	0.209	0.197
35.659 ⁽¹¹⁸⁾	35.749 ⁽¹¹⁶⁾	0.090	0.085

B. Exaltations of Styrene, α -Methylstyrene, Propenylbenzene, and Allylbenzene

The introduction of a methyl group in the α -position of styrene destroys the coplanarity and inhibits resonance as evidenced by the lowering of the molecular exaltation (112), as shown in Table 2, and by its influence on the ultraviolet absorption spectrum of styrene (43); the introduction of a methyl group in the β -position of styrene

has little influence on the ultraviolet absorption spectrum of styrene. The lower exaltation of the *cis*-isomer of propenylbenzene is due to steric inhibition of resonance, while the lack of exaltation in allylbenzene is due to non-conjugation of the allyl double bond with the ring.

TABLE 2

EXALTATIONS OF STYRENE, α -METHYLSTYRENE,
PROPENYLBENZENE, AND ALLYLBENZENE

Compound	MR _D		EM _D	EZ _D
	Calc.	Obsd.		
Styrene ($C_6H_5CH=CH_2$)	35.076	36.470 ⁽²⁷⁾	1.394	1.340
α -Methylstyrene ($C_6H_5\underset{\text{CH}_3}{\underset{ }{C}}=CH_2$)	39.694	40.642 ⁽²⁷⁾	0.948	0.802
Propenylbenzene ($C_6H_5CH=CHCH_3$)	39.694	41.129 ⁽⁶³⁾	1.435	1.214
		41.310 ⁽¹⁴⁾	1.616	1.368
	<u>cis</u>	40.716 ⁽⁷⁹⁾	1.022	0.865
	<u>trans</u>	41.574 ⁽⁷⁹⁾	1.880	1.591
Allylbenzene ($C_6H_5CH_2CH=CH_2$)	39.694	39.691 ⁽¹¹⁹⁾	-0.003	-0.003

Since both α -methylstyrene and trans-propenylbenzene polymerize less readily than styrene, it is not possible, from these data, to correlate the exaltation with polymerization ability.

C. Exaltations of Methylstyrenes

The absolute rates of polymerization of m-methylstyrene and p-methylstyrene are greater than that of styrene (53). Data in Table 3 show that correlation of exaltations with polymerization rates appears to be rather satisfactory in the case of molecular exaltations, but less satisfactory when specific exaltations are used.

TABLE 3
EXALTATIONS OF METHYLSTYRENES

Compound	MR_D		EM_D	$E\Sigma_D$
	Calcd.	Obsd.		
Styrene	35.076	36.470(27)	1.394	1.340
<u>m</u> -Methylstyrene	39.694	41.321(24,86)	1.627	1.377
<u>p</u> -Methylstyrene	39.694	41.128(24,27)	1.434	1.213

D. Exaltations of Monochlorostyrenes

Monochlorostyrenes thermally polymerize at a rate approximately eight times as fast as styrene, and approximately three times as fast as styrene when benzoyl peroxide is used as the initiator; the following order of rates was established for the individual monochlorostyrenes (60, 115).



On the basis of data shown in Table 4, there again appears to be no correlation of exaltations with polymerization rates.

TABLE 4

EXALTATIONS OF MONOCHLOROSTYRENES

Compound	MR_D		EM_D	E^1_D
	Calcd.	Obsd.		
Styrene	35.076	36.470 ⁽²⁷⁾	1.394	1.340
<u>o</u> -Chlorostyrene	39.943	40.989 ^(12,124)	1.046	0.755
<u>m</u> -Chlorostyrene	39.943	41.090 ^(12,29,70,114,124)	1.147	0.828
<u>p</u> -Chlorostyrene	39.943	41.657 ^(12,27,70)	1.714	1.237

E. Exaltations of Dichlorostyrenes

Dichlorostyrenes polymerize much faster than styrene, (78), and thermally polymerize faster than the monochlorostyrenes, with 2,5-dichlorostyrene faster than 2,4-dichlorostyrene, which in turn was faster than 3,4-dichlorostyrene (61); there appeared to be no correlation of activation energies and rates of polymerization.

On the basis of data shown in Tables 4 and 5, there appears to be no correlation of exaltations with polymerization rates.

TABLE 5
EXALTATIONS OF DICHLOROSTYRENES

Compound	MR _D		EM _D	EΣ _D
	Calcd.	Obsd.		
Styrene	35.076	36.470 (27)	1.394	1.340
2,3-Dichloro- styrene	44.810	45.162 (67,68,78)	0.352	0.203
2,4-Dichloro- styrene	44.810	46.324 (61,62,67 68,78,124)	1.514	0.875
2,5-Dichloro- styrene	44.810	46.138 (12,61,62, 78)	1.328	0.767
2,6-Dichloro- styrene	44.810	45.258 (67,68,78)	0.448	0.259
3,4-Dichloro- styrene	44.810	46.274 (12,33,61, 62,67,68, 78,124)	1.464	0.846
3,5-Dichloro- styrene	44.810	46.647 (67,68,78)	1.837	1.062

F. Exaltations of p-Ethylstyrene and
p-tert-Butylstyrene

The polymerization of styrene, p-methylstyrene, p-ethylstyrene, and p-tert-butylstyrene using 2,2'-azobis-isobutyronitrile as initiator (49) showed the initial rate of polymerization (R_0) to be noticeably increased in the case of p-methylstyrene by the addition of N,N-dimethylaniline (DMA); this was ascribed to the hyperconjugation effect.

Data in Table 6 show no correlation of exaltations with polymerization rates.

TABLE 6
EXALTATIONS OF p-ETHYLSTYRENE
AND p-tert-BUTYLSTYRENE

Compound	MR _D		R ₀		EM _D	EΣ _D
	Calcd.	Obsd.	---	DMA		
Styrene	35.076	36.470 ⁽²⁷⁾	0.51	0.51	1.394	1.340
<u>p</u> -Methylstyrene	39.694	41.128 ⁽²⁷⁾ (24)	0.49	0.58	1.434	1.213
<u>p</u> -Ethylstyrene	44.312	46.312 ⁽²⁷⁾	0.44	0.47	2.000	1.513
<u>p-tert</u> -Butylstyrene	53.548	54.239 ⁽³²⁾	0.41	0.43	0.691	0.432

CHAPTER III

INVESTIGATION OF POSSIBLE CORRELATION OF THE EXALTATION OF REFRACTION WITH THE RATE OF POLYMERIZATION IN FREE RADICAL COPOLYMERIZATIONS

At this point it was apparent that there was little, if any, correlation of the exaltation of refraction with the rate of polymerization in homopolymerizations. The next step was to investigate the possible correlation in copolymerizations.

Since data on free radical copolymerizations were much more extensive than those on ionic copolymerizations (75), it was decided to examine first those free radical copolymerizations involving similar and dissimilar comonomers.

The following section deals with the copolymerization of styrene, methyl methacrylate, and maleic anhydride with substituted styrenes, and the correlation of the relative reactivity of the substituted styrenes toward the styrene, methyl methacrylate, and maleic anhydride radicals with both Hammett's sigma value (40, 77, 102, 103) for the substituent on the substituted comonomer, and the differences existing in either the exaltations of the comonomers or the exaltations of the substituted and

unsubstituted styrenes.

A. Copolymerization of Styrene with Substituted Styrenes

Walling et al. (121, 122) have determined the relative reactivity toward the styrene type radical for a number of substituted styrenes, and have demonstrated a correlation between these relative reactivities and the Hammett sigma value of the styrene substituents. Insofar as data were available for the calculation of exaltations, it has been possible, with one exception, to show rather good correlation of the differences existing between the specific exaltation of styrene and the substituted styrenes ($\Delta E\Sigma_D$) with the logarithm of the relative reactivity ($-\log r_1$) toward the styrene radical for these substituted styrenes.

Table 7 summarizes these data, while Figure 1 is a plot of the logarithms of the relative reactivities of these substituted styrenes versus $\Delta E\Sigma_D$ and σ , Hammett's substituent value.

B. Copolymerization of Methyl Methacrylate with Substituted Styrenes

Walling et al. (121, 122) have determined the relative reactivity toward the methyl methacrylate radical for a number of substituted styrenes, and plotted the logarithms

TABLE 7

RELATIVE REACTIVITIES AND EXALTATIONS FOR THE COPOLYMERIZATION OF
STYRENE (M_1) WITH SUBSTITUTED STYRENES (M_2)

Substituent	$-\log r_2$	EM_D	$E \Sigma D$	ΔEM_D	$\Delta E \Sigma D$	σ^-
p-NO ₂	0.722	0.000 (31)	0.000	1.394	1.340	1.27
m-Br	0.260	0.963 (13, 124)	0.526	0.431	0.814	0.391
o-Cl	0.252	1.046 (12, 124)	0.755	0.348	0.585	---
m-Cl	0.193	1.147 (12, 29, 70, 114, 124)	0.828	0.247	0.512	0.373
p-Br	0.158	1.634 (27, 71, 86, 99, 122)	0.893	-0.240	0.447	0.232
p-Cl	0.132	1.714 (12, 27, 70)	1.237	-0.320	0.103	0.227
None	0.000	1.394 (27)	1.340	0.000	0.000	0.000
p-NMe ₂	-0.006	3.993 (37, 86)	2.712	-2.599	-1.372	-0.205
p-OMe	-0.065	2.298 (36, 59, 72, 81, 86, 93, 99, 108, 124)	1.713	-0.904	-0.373	-0.268

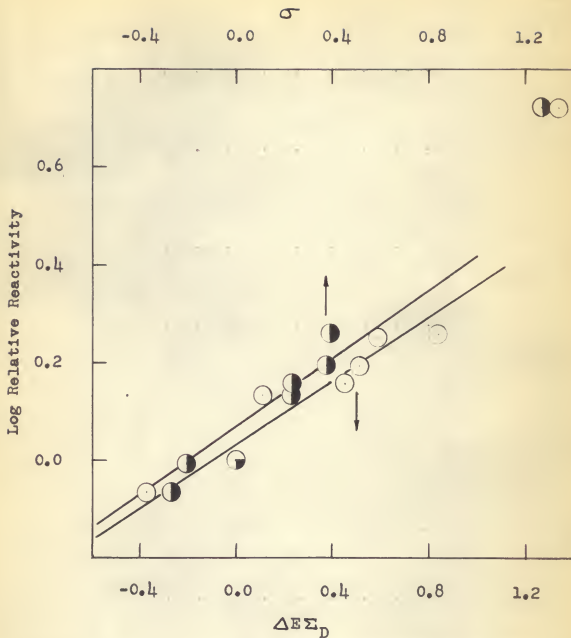


Fig. 1.--Plot of the logarithms of relative reactivities of substituted styrenes with the styrene radical versus the differences existing between the specific exaltations of styrene and the substituted styrenes, and Hammett's sigma value for the substituent.

of these relative reactivities against the Hammett sigma value for the styrene substituents; the fit to a straight line was reasonably good, with the exception of *p*-methoxy-, *p*-dimethylamino-, and *p*-methylstyrenes. Table 8 shows Walling's values for the relative reactivities of styrene and several substituted styrenes toward the methyl methacrylate radical, the molecular exaltations for these styrenes, and ΔE_{M_D} which represents the molecular exaltations of the substituted styrenes less the molecular exaltation for styrene.

The correlation of relative reactivities with the differences existing between the molecular exaltation of methyl methacrylate (19, 35, 70, 74, 120) and the molecular exaltations of the styrenes ($\Delta E_{M_D}^1$) was also quite good; less than satisfactory, however, were the correlations of relative reactivities with the differences existing between the specific exaltation of substituted styrenes and styrene (ΔE_{S_D}) and with the differences existing between the specific exaltations of the styrenes and methyl methacrylate.

Figure 2 is a plot of the logarithms of the relative reactivities of these substituted styrenes against ΔE_{M_D} .

TABLE 8

RELATIVE REACTIVITIES AND EXALTATIONS FOR THE
COPOLYMERIZATION OF METHYL METHACRYLATE
WITH SUBSTITUTED STYRENES

Substituent	$-\log r_1$	EM_D	EX_D	ΔEM_D	ΔEM_D^1
p-Me ₂	0.699	3.993 ^(37,86)	2.712	2.599	3.791
		(36,59,72) (81,86,93) (99,108) (124)			
p-OMe	0.538	2.298	1.713	0.904	2.096
		(27,71,86)			
p-Br	0.398	1.634 ^(99,122)	0.893	0.240	1.432
		(24,27)			
p-Me	0.398	1.434 ^(24,27)	1.213	0.040	1.232
None	0.337	1.394 ⁽²⁷⁾	1.340	0.000	1.192
p-Cl	0.377	1.714 ^(12,27,70)	1.237	0.320	1.512
		(12,29,70)			
m-Cl	0.328	1.147 ^(114,124)	0.828	-0.247	0.945
		(13,124)			
m-Br	0.319	0.963 ^(13,124)	0.526	-0.431	0.761
o-Cl	0.301	1.046 ^(12,124)	0.755	-0.348	0.844
m-Me	0.276	1.627 ^(24,86)	1.377	-0.233	1.425

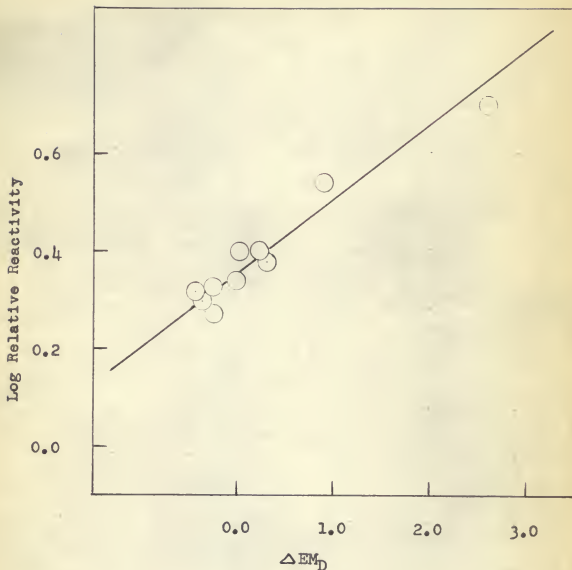


Fig. 2.--Plot of the logarithms of relative reactivities of styrene and several substituted styrenes toward the methyl methacrylate radical versus the differences existing between the molecular exaltations of the substituted styrenes and the molecular exaltation of styrene.

C. Copolymerization of Maleic Anhydride
with Substituted α -Methylstyrenes

Walling et al. (123) have determined the relative reactivity toward the maleic anhydride type radical for α -methylstyrene and a number of substituted α -methylstyrenes, and found that the relative reactivities showed little relation to the Hammett sigma values of the substituents. The α -methylstyrenes studied by Walling are reported to be liquids with the exception of *N,N*-dimethyl-*p*-isopropenylaniline (98), and *p*-isopropenylanisole (10) which is reported to be both a solid (9, 98) and a liquid (44), with the implication (44) that the liquid is the monomer and the solid is the dimer.

Table 9 shows Walling's values for the relative reactivities of α -methylstyrene and substituted α -methylstyrenes toward the maleic anhydride radical, the exaltations for the α -methylstyrenes, and the differences existing between the molecular exaltations (ΔE_M^D) and the specific exaltations (ΔE_S^D) of the substituted α -methylstyrenes and α -methylstyrene. Figure 3 is a plot of the logarithms of the relative reactivities of these α -methylstyrenes against ΔE_S^D . Walling's relative reactivities also show little relation to the differences existing between the specific and molecular exaltations of α -methylstyrene and the substituted α -methylstyrenes.

TABLE 9

RELATIVE REACTIVITIES AND EXALTATIONS FOR THE
COPOLYMERIZATION OF MALEIC ANHYDRIDE WITH
SUBSTITUTED α -METHYLSTYRENES

Substituent	$-\log r_1$	EM_D	EZ_D	ΔEM_D	ΔEZ_D
p-Me	0.236	$1.270^{(2,7,38)}$ $^{(90,123)}$	0.961	0.321	0.159
None	0.000	$0.949^{(6,7)}$ $^{(27,42)}$	0.803	0.000	0.000
m-Br	-0.018	$0.770^{(98)}$	0.391	-0.179	-0.412
p-CN	-0.018	$2.713^{(98,118)}$	1.895	1.764	1.092
p-Cl	-0.102	$0.958^{(7,98)}$	0.628	0.009	-0.175
p-Br	-0.137	$0.918^{(10,98)}$	0.466	-0.031	-0.337
p-F	-0.143	$0.851^{(98,118)}$	0.625	-0.098	-0.178

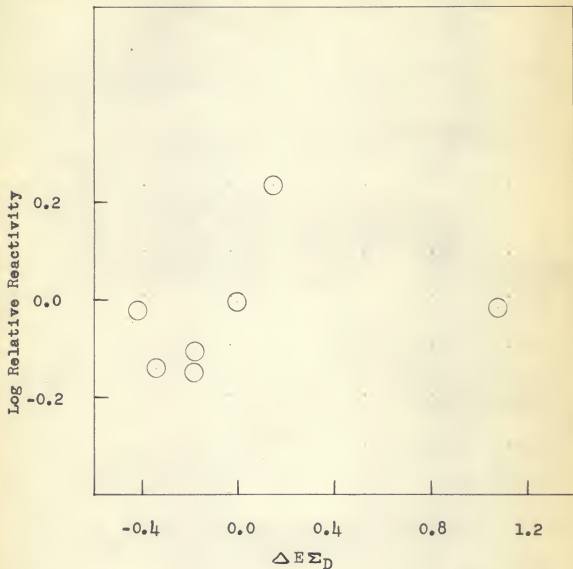


Fig. 3.--Plot of the logarithms of relative reactivities of α -methylstyrene and several substituted α -methylstyrenes toward the maleic anhydride radical versus the differences existing between the specific exaltations of the substituted α -methylstyrenes and the specific exaltation of α -methylstyrene.

CHAPTER IV

INVESTIGATION OF POSSIBLE CORRELATION OF THE EXALTATION OF REFRACTION WITH THE RATE OF POLYMERIZATION IN IONIC COPOLYMERIZATIONS

At this point it was apparent that there was a definite correlation of exaltation of refraction with the rate of polymerization in free radical polymerizations involving similar comonomers, and the free radical copolymerizations utilizing maleic anhydride were to be avoided.

The following section deals with the ionic copolymerization of styrene with substituted styrenes, and the correlation of the relative reactivity of the substituted styrenes toward the styrene radical with the differences existing in the exaltations of the comonomers.

A. Copolymerization of Styrene with Substituted Styrenes

Overberger et al. (86) have determined the relative reactivity toward the styrene carbonium ion for several substituted styrenes, and showed a definite correlation between these relative reactivities and the Hammett sigma values of the styrene substituents. Table 10 shows Overberger's values for the relative reactivities of substituted styrenes toward the styrene carbonium ion, the

exaltations of the substituted styrenes, and the differences existing between the molecular exaltations (ΔEM_D) and the specific exaltations ($\Delta E\Sigma_D$) of the substituted styrenes and styrene. Although index of refraction data are available for m-nitrostyrene (69, 86, 114, 128), no density data could be found; for this reason, m-nitrostyrene was not included in Table 10.

Figure 4 is a plot of the logarithms of the relative reactivities of these substituted styrenes against ΔEM_D ; an equally good curve was obtained when $-\log r_1$ was plotted against $\Delta E\Sigma_D$.

TABLE 10

RELATIVE REACTIVITIES AND EXALTATIONS FOR THE CATION-CATALYZED COPOLYMERIZATION OF STYRENE WITH SUBSTITUTED STYRENES

Substituent	$-\log r_1$	EM_D	$E\Sigma_D$	ΔEM_D	$\Delta E\Sigma_D$
p-OMe	2.0	2.298 ^(36,59) ₍₇₂₎	1.713	0.904	0.373
<u>m</u> -OMe	0.045	1.793 ^(36,59) _(86,108)	1.336	0.399	-0.004
p-Cl	-0.39	1.714 ^(12,27) ₍₇₀₎	1.237	0.320	-0.103
None	----	1.394 ⁽²⁷⁾	1.340	0.000	0.000
<u>m</u> -Cl	-0.52	1.147 ^(12,29,70) _(114,124)	0.828	0.247	-0.512

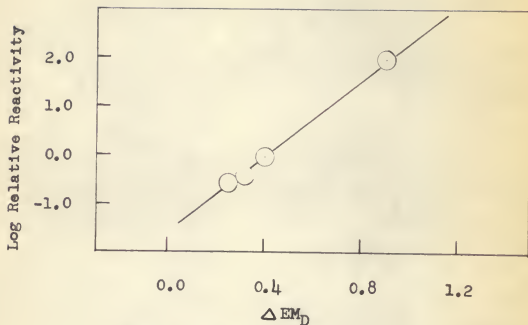


Fig. 4.--Plot of the logarithms of relative reactivities of styrene and several substituted styrenes toward the styrene carbonium ion versus the differences existing between the molecular exaltations of the substituted styrenes and styrene.

B. Copolymerization of p-Chlorostyrene
with Substituted Styrenes

Overberger et al. (86) have determined the relative reactivity toward the p-chlorostyrene carbonium ion for several substituted styrenes, and noted a definite correlation between these relative reactivities and the Hammett sigma values of the styrene substituents; other data on ionic polymerizations may be found in a review by Pepper (88). Table 11 shows Overberger's values for the relative reactivities of styrene and substituted styrenes toward the p-chlorostyrene carbonium ion, the exaltations of the styrenes, and the differences existing between the molecular exaltations (ΔE_{MD}) and the specific exaltations (ΔE_{SD}) of the substituted styrenes and p-chlorostyrene.

Figure 5 is a plot of the logarithms of the relative reactivities of these substituted styrenes against ΔE_{SD} ; no correlation existed when $-\log r_1$ was plotted against ΔE_{MD} .

TABLE 11

RELATIVE REACTIVITIES AND EXALTATIONS FOR THE CATION-
CATALYZED COPOLYMERIZATION OF *p*-CHLOROSTYRENES
WITH SUBSTITUTED STYRENES

Substituent	$-\log r_1$	EM_D	$E\mathcal{Z}_D$	ΔEM_D	$\Delta E\mathcal{Z}_D$
<i>p</i> -Me	0.658	1.434 ^(24,27)	1.213	-0.280	0.024
<i>p</i> -H	0.447	1.394 ⁽²⁷⁾	1.340	-0.320	-0.103
<i>m</i> -OMe	0.420	1.793 ^{(36,59) (86,108)}	1.336	0.079	-0.099
<i>p</i> -Br	0.0	1.634 ^{(27,71,86) (99,122)}	0.893	-0.080	-0.344
<i>p</i> -Cl	----	1.714 ^(12,27,70)	1.237	0.000	0.000

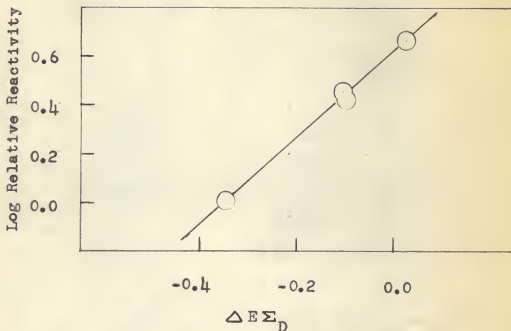


Fig. 5.--Plot of the logarithms of relative reactivities of styrene and several substituted styrenes toward the *p*-chloro-styrene carbonium ion versus the differences existing between the specific exaltations of the substituted styrenes and *p*-chloro-styrene.

CHAPTER V

PREPARATION OF ALLYL AROMATIC ETHERS

Since data in the previous sections showed it possible to correlate both Hammett's sigma values and the molecular and specific exaltations with relative reactivities in free radical and ionic copolymerizations involving rather similar comonomers, it was now necessary to prepare a number of allyl aromatic ethers in order to determine their specific and molecular exaltations, and to attempt to correlate these exaltations with Hammett's sigma values for the ring substituents. With the exception of allyl phenyl ether, phenyl propyl ether, allyl 3,4-xylyl ether, and allyl o-chlorophenyl ether, data were not available for the calculation of the exaltations of the other fourteen ethers described in this section; allyl m-chlorophenyl ether and allyl m-bromophenyl ether were not described in the literature.

Of the several other compounds which could have conceivably been included in this series, allyl m-nitrophenyl ether is a solid (m.p. 31.5-32.0° (129)), p-(allyloxy)-aniline is quite unstable (22, 39, 105), and p-(allyloxy)-benzonitrile is a solid (m.p. 43° (87)).

A. Nomenclature

All nomenclature in this work will follow that used by Chemical Abstracts.

B. Materials

Allyl phenyl ether, phenyl propyl ether, *p*-chlorophenol, *m*-methoxyphenol, and *m*-bromophenol were Eastman Grade, purchased from the Eastman Kodak Company; *o*-chlorophenol, *p*-chlorophenol, *p*-methoxyphenol, *p*-cresol, *m*-cresol, *p*-bromophenol, and 3,4-xylenol were Best Grade, purchased from Matheson Coleman and Bell; *o*-cresol, and *p*-nitrophenol were Practical Grade, purchased from Matheson Coleman and Bell; *p*-*tert*-butylphenol and *p*-hydroxyacetophenone were provided by the Dow Chemical Company; 2,4-dichlorophenol was purchased from Brothers Chemical Company; *p*-(allyloxy)-benzaldehyde was furnished by Dr. G. B. Butler, Department of Chemistry, University of Florida; allyl bromide was purchased from the Shell Chemical Corporation.

C. Physical Measurements

The ethers were prepared under anhydrous conditions according to Claisen and Eisleb (21), or in aqueous sodium hydroxide according to Tarbell and Wilson (110). Although the yields of crude products were nearly quantitative in most cases, a reasonably narrow cut of carefully fractionated

product was taken for the physical measurements, which were made on the freshly fractionated compounds. Pressures below 10 mm. were read on a McLeod gauge, and other pressures were read on a Zimmerli gauge; temperatures are °C., and are uncorrected.

The refractive indexes were measured by means of a Bausch and Lomb precision refractometer in which thermostated water was circulated through the prism blocks. The temperature of the prisms was maintained constant within $\pm 0.02^\circ$. A sodium vapor lamp was used as the light source.

Densities were determined on approximately 10 ml. samples, and all weighings were made on an analytical balance sensitive to 0.1 mg.

D. Preparations

1. Allyl phenyl ether ($C_6H_5OCH_2CH=CH_2$)

Carefully fractionated allyl phenyl ether exhibited the following constants: m.p. -47.0° ; b.p. 61.0° at 6.5 mm. (reported: 73° at 11 mm. (22), $80-84^\circ$ at 13 mm. (32), $93-94^\circ$ at 26 mm. (95), $112-113^\circ$ at 34 mm. (47)); n_D^{25} 1.51935 (reported: n_D^{20} 1.52232 (117), n_D^{20} 1.5218 (32), n_D^{21} 1.5208 (47)); d_4^{25} 0.97580 (reported: d_4^{15} 0.9832 (95), d_{15}^{15} 0.9845 (22), $d_4^{25.4}$ 0.9762 (117)). MR_D 41.749, calcd. 41.337; EM_D 0.412; EZ_D 0.308.

2. Phenyl propyl ether ($C_6H_5OCH_2CH_2CH_3$)

Carefully fractionated phenyl propyl ether exhibited the following constants: b.p. 189° at 762 mm. (reported: 187° at 751 mm. (117), 189.9° at 760 mm. (27)); n_D^{25} 1.49863 (reported: n_D^{20} 1.50106 (27), n_D^{20} 1.51034 (117), n_D^{25} 1.49881 (27)); d_4^{25} 0.94342 (reported: d_4^{20} 0.94743 (27), d_4^{20} 0.9494 (117), d_4^{25} 0.94295 (27)). MR_D 42.367, calcd. 41.804; EM_D 0.563; EX_D 0.414.

3. Allyl p-chlorophenyl ether ($p\text{-ClC}_6\text{H}_4\text{OCH}_2\text{CH}=\text{CH}_2$)

Allyl bromide (66.6 g., 0.55 mole), 64.3 g. (0.50 mole) of p-chlorophenol, 76.0 g. (0.55 mole) anhydrous potassium carbonate in 37.8 g. acetone were refluxed for 11.0 hours. After water was added, the oil layer which formed was separated from the water layer, and the latter layer was extracted with two 100-ml. portions of ether; the oil and ether extracts were combined, washed with 5% aqueous sodium hydroxide, then water, and dried over anhydrous potassium carbonate. On fractionation of the crude product (80.7 g., 95.8%), allyl p-chlorophenyl ether 61.8 g., 73.4% was obtained as a clear, water-white oil, b.p. $90\text{--}91^\circ$ at 6.0 mm. (reported: $106\text{--}107^\circ$ at 12 mm. (21)); n_D^{25} 1.53468, d_4^{25} 1.12328 (reported: d_4^{15} 1.131 (21)); MR_D 46.718, calcd. 46.204; EM_D 0.514; EX_D 0.305.

4. Allyl m-chlorophenyl ether ($\underline{m}\text{-ClC}_6\text{H}_4\text{OCH}_2\text{CH=CH}_2$)

Allyl bromide (75.8 g., 0.625 mole), 64.3 g. (0.5 mole) m-chlorophenol, 22.5 g. (0.56 mole) sodium hydroxide in 125 ml. water and 250 ml. acetone were refluxed for one hour. After water was added and the mixture extracted with ether, the ether extracts were washed with 5% aqueous sodium hydroxide, then water, and dried over anhydrous potassium carbonate. On fractionation of the crude product (84.5 g., 100%), allyl m-chlorophenyl ether (58.2 g., 69.1%) was obtained as a clear, water-white oil, b.p. 87.0-87.5° at 6.0 mm., n_D^{25} 1.53384, d_4^{25} 1.12195; M_{rD} 46.710, calcd. 46.204; EM_{D} 0.506; EZ_{D} 0.300.

5. Allyl o-chlorophenyl ether ($\underline{o}\text{-ClC}_6\text{H}_4\text{OCH}_2\text{CH=CH}_2$)

Allyl bromide (75.8 g., 0.625 mole), 64.3 g. (0.5 mole) m-chlorophenol, 22.5 g. (0.56 mole) sodium hydroxide in 125 ml. water and 250 ml. acetone were refluxed for one hour. After water was added and the mixture extracted with ether, the ether extracts were washed with 5% aqueous sodium hydroxide, then water, and dried over anhydrous potassium carbonate. On fractionation of the crude product (81.8 g., 97.0%), allyl o-chlorophenyl ether (52.6 g., 62.5%) was obtained as a clear,

water-white oil (yellowed on standing), b.p. 92.5-93.0° at 6.5 mm. (reported: 108-110° at 12 mm. (16), 108-110° at 15 mm. (110), 118-120° at 25 mm. (34)); n_D^{25} 1.53744 (reported: n_D^{25} 1.5388 (110)); d_4^{25} 1.12322 (reported: d_4^{15} 1.133 (34), d_{25}^{25} 1.132 (110)); MR_D 46.918, calcd. 46.204; EM_D 0.714; EZ_D 0.423.

6. Allyl p-tolyl ether ($p\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_2\text{CH=CH}_2$)

Allyl bromide (113.5 g., 0.94 mole), 81.0 g. (0.75 mole) p-cresol, 33.6 g. (0.84 mole) sodium hydroxide in 190 ml. water and 375 ml. acetone were refluxed for one hour. Acetone (325 ml.) was removed at atmospheric pressure to a maximum vapor temperature of 68°. After water was added, the oil layer which formed was separated from the water layer, and the latter layer was extracted with ether; the oil and ether extracts were combined, washed with 5% aqueous sodium hydroxide, then water, and dried over anhydrous potassium carbonate. On fractionation of the crude product (103.0 g., 92.8%), allyl p-tolyl ether (82.7 g., 74.5%) was obtained as a clear, water-white oil, b.p. 72-73° at 4.8 mm. (reported: 65 ± 1° at 4 mm. (58), 91° at 12 mm. (21), 91-92° at 12 mm. (23), 97-98° at 16 mm. (48), 212.5-216.5° at 760 mm. (89)); n_D^{25} 1.51523, d_4^{25} 0.96133 (reported: d_4^{15} 0.967 (21), d_{25}^{25} 0.9662 (89), d_4^{35} 0.9494 (58)); MR_D 46.508, calcd. 45.955; EM_D 0.553; EZ_D 0.374.

7. Allyl m-tolyl ether (m-CH₃C₆H₄OCH₂CH=CH₂)

Allyl bromide (113.5 g., 0.94 mole), 81.0 g. (0.75 mole) m-cresol, 33.6 g. (0.84 mole) sodium hydroxide in 190 ml. water and 375 ml. acetone were refluxed for one hour. Acetone (330 ml.) was removed at atmospheric pressure to a maximum vapor temperature of 71°. After water was added, the oil layer which formed was separated from the water layer, and the latter layer was extracted with ether; the oil and ether extracts were combined, washed with 5% aqueous sodium hydroxide, then water, and dried over anhydrous potassium carbonate. On fractionation of the crude product (98.8 g., 89.0%), allyl m-tolyl ether (73.9 g., 65.6%) was obtained as a clear, water-white oil, b.p. 80-81° at 7.0 mm. (reported: 92-94° at 12 mm. (21)); n_D^{25} 1.51607, d_4^{25} 0.96188 (reported: d_4^{25} 0.965 (21)); MR_D 46.544, calcd. 45.955; EM_D 0.589; EX_D 0.398.

8. Allyl o-tolyl ether (o-CH₃C₆H₄OCH₂CH=CH₂)

Allyl bromide (113.5 g., 0.94 mole), 81.0 g. (0.75 mole) o-cresol, 33.6 g. (0.84 mole) sodium hydroxide in 190 ml. water and 375 ml. acetone were refluxed for one hour. Acetone (325 ml.) was removed at atmospheric pressure to a maximum vapor temperature of 70°. After water was added, the oil layer which formed was separated from the

water layer, and the latter layer was extracted with ether; the oil and ether extracts were combined, washed with 5% aqueous sodium hydroxide, then water, and dried over anhydrous potassium carbonate. On fractionation of the crude product (97.7 g., 88.0%), allyl *o*-tolyl ether (73.3 g., 66.1%) was obtained as a clear, water-white oil, b.p. 75.0-75.5° at 7.0 mm. (reported: 85° at 12 mm. (21), 104° at 26 mm. (95)); n_D^{25} 1.51672 (reported: $n_D^{18.4}$ 1.51876 (5)), d_4^{25} 0.96476 (reported: d_4^{18} 0.969 (21), d_4^{18} 0.9698 (95), $d_4^{18.4}$ 0.9687 (5)); M_{rD} 46.456, calcd. 45.955; EM_D 0.501; BE_D 0.338.

9. Allyl *p*-bromophenyl ether ($p\text{-BrC}_6\text{H}_4\text{OCH}_2\text{CH}=\text{CH}_2$)

Allyl bromide (75.8 g., 0.625 mole), 86.5 g. (0.5 mole) *p*-bromophenol, 22.5 g. (0.56 mole) sodium hydroxide in 125 ml. water and 250 ml. acetone were refluxed for one hour. Acetone (225 ml.) was removed at atmospheric pressure to a maximum vapor temperature of 74°. After water was added, the oil layer which formed was separated from the water layer, and the latter layer was extracted with ether; the oil and ether extracts were combined, washed with 5% aqueous sodium hydroxide, then water, and dried over anhydrous potassium carbonate. On fractionation of the crude product (103.0 g., 96.6%), allyl *p*-bromophenyl ether (84.9 g., 79.6%) was obtained

as a clear, water-white oil, b.p. 98.5-99.0° at 4.7 mm.
(reported: 126° at 14 mm. (21)), n_D^{25} 1.55793, d_4^{25} 1.38499;
 MR_D 49.596, calcd. 49.102; EM_D 0.494; $E\alpha_D$ 0.232.

10. Allyl m-bromophenyl ether (m-BrC₆H₄OCH₂CH=CH₂)

Allyl bromide (46.0 g., 0.38 mole), 52.0 g. (0.30 mole) m-bromophenol, 13.6 g. (0.34 mole) sodium hydroxide in 75 ml. water and 150 ml. acetone were refluxed for one hour. Acetone (125 ml.) was removed at atmospheric pressure to a maximum vapor temperature of 73°. After water was added, the oil layer which formed was separated from the water layer, and the latter layer was extracted with ether; the oil and ether extracts were combined, washed with 5% aqueous sodium hydroxide, then water, and dried over anhydrous potassium carbonate. On fractionation of the crude product (62.2 g., 97.4%), allyl m-bromophenyl ether (50.5 g., 79.1%) was obtained as a clear, water-white oil, b.p. 95.0-96.0° at 4.5 mm., n_D^{25} 1.55716, d_4^{25} 1.38234; MR_D 49.636, calcd. 49.102; EM_D 0.534; $E\alpha_D$ 0.251.

11. Allyl 3,4-xylyl ether (3,4-Me₂C₆H₃OCH₂CH=CH₂)

Allyl bromide (113.5 g., 0.94 mole), 91.6 g. (0.75 mole) 3,4-xylenol, 33.6 g. (0.84 mole) sodium hydroxide in 190 ml. water and 375 ml. acetone were refluxed for one

hour. Acetone (325 ml.) was removed at atmospheric pressure to a maximum vapor temperature of 69° . After water was added, the oil layer which formed was separated from the water layer, and the latter layer was extracted with ether; the oil and ether extracts were combined, washed with 5% aqueous sodium hydroxide, then water, and dried over anhydrous potassium carbonate. On fractionation of the crude product (114.4 g., 94.2%), allyl 3,4-xylyl ether (74.5 g., 61.3%) was obtained as a clear, water-white oil, b.p. $79.5-80.5^{\circ}$ at 3.0 mm. (reported: $75-79^{\circ}$ at 3.0 mm. (66)), n_D^{25} 1.51951 (reported: n_D^{20} 1.5200 (66)); d_4^{25} 0.96204 (reported: d_4^{20} 0.9543 (66)); MR_D 51.225, calcd. 50.573; EM_D 0.652; E_D^{25} 0.402.

12. Allyl 2,4-dichlorophenyl ether ($2,4-Cl_2C_6H_3OCH_2CH=CH_2$)

Allyl bromide (75.8 g., 0.625 mole), 81.5 g. (0.5 mole) 2,4-dichlorophenol, 22.5 g. (0.56 mole) sodium hydroxide in 125 ml. water and 250 ml. acetone were refluxed for one hour. Acetone (225 ml.) was removed at atmospheric pressure to a maximum vapor temperature of 76° . After water was added, the oil layer which formed was separated from the water layer, and the latter layer was extracted with ether; the oil and ether extracts were combined, washed with 5% aqueous sodium hydroxide, then water,

and dried over anhydrous potassium carbonate. On fractionation of the crude product (101.6 g., 100%), allyl 2,4-dichlorophenyl ether (71.2 g., 70.1%) was obtained as a clear, water-white oil (yellowed on standing), b.p. 106.5-107.5° at 4.8 mm. (reported: 144-145° at 25 mm. (94)); n_D^{25} 1.55196, d_4^{25} 1.25502; MR_D 51.699, calcd. 51.071; EM_D 0.628; E_D^{25} 0.310.

13. Allyl p-tert-butylphenyl ether (p-tert- $BuC_6H_4OCH_2CH=CH_2$)

Allyl bromide (75.1 g., 0.62 mole), 75.1 g. (0.50 mole) p-tert-butylphenol, 90.0 g. (0.65 mole) anhydrous potassium carbonate in 225 ml. acetone were refluxed for fifteen hours. After water was added, the oil layer which formed was separated from the water layer, and the latter layer was extracted with ether; the oil and ether extracts were combined, washed with 5% aqueous sodium hydroxide, then water, and dried over anhydrous potassium carbonate. On fractionation of the crude product (87.6 g., 92.1%), allyl p-tert-butylphenyl ether (60.2 g., 63.2%) was obtained as a clear, water-white oil, m.p. 16.8°, b.p. 109.0-109.5° at 6.5 mm. (reported: 115-116° at 3.0 mm. (97), 138-139° at 10.0 mm. (16)); n_D^{25} 1.50660 (reported: n_D^{25} 1.5065 (97)), d_4^{25} 0.93460; MR_D 60.548, calcd. 59.809; EM_D 0.739; E_D^{25} 0.388.

14. 1-(Allyloxy)-4-methoxybenzene ($\underline{p}$ -MeOC₆H₄OCH₂CH=CH₂)

Allyl bromide (99.9 g., 0.825 mole), 93.0 g. (0.75 mole) $\underline{p}$ -methoxyphenol, 104.0 g. (0.75 mole) anhydrous potassium carbonate in 150 ml. acetone were refluxed eight hours. After water was added, the oil layer which formed was separated from the water layer, and the latter layer was extracted with ether; the oil and ether extracts were combined, washed with 5% aqueous sodium hydroxide, then water, and dried over anhydrous potassium carbonate. On fractionation of the crude product (116.4 g., 94.5%), 1-(allyloxy)-4-methoxybenzene (87.6 g., 71.3%) was obtained as a clear, water-white oil, b.p. 113.0-113.5° at 9.5 mm. (reported: 119-120° at 13 mm. (73)); n_D^{25} 1.52509; d_4^{25} 1.04258; MR_D 48.273, calcd. 47.598; EM_D 0.675; $E\alpha_D$ 0.411.

15. 1-(Allyloxy)-3-methoxybenzene ($\underline{m}$ -MeOC₆H₄OCH₂CH=CH₂)

Allyl bromide (59.0 g., 0.48 mole), 55.0 g. (0.44 mole) $\underline{m}$ -methoxyphenol, 61.5 g. (0.44 mole) anhydrous potassium carbonate in 90 ml. acetone were refluxed eight hours. After water was added, the oil layer which formed was separated from the water layer, and the latter layer was extracted with ether; the oil and ether extracts were combined, washed with 5% aqueous sodium hydroxide (first

wash was intensely green in color), then water, and dried over anhydrous potassium carbonate. On fractionation of the crude product (66.2 g., 91.0%), 1-(allyloxy)-3-methoxybenzene (40.4 g., 55.6%) was obtained as a clear, very faintly yellow oil, b.p. 122-123° at 14 mm. (reported: 125-126° at 15 mm. (73)). Refractionation still gave a faintly yellow product, b.p. 96.0° at 4.3 mm.; n_D^{25} 1.52618; d_4^{25} 1.04110; MR_D 48.427, calcd. 47.598; EM_D 0.829; EZ_D 0.505.

16. p-(Allyloxy)benzaldehyde ($p\text{-CH}_2=\text{CHCH}_2\text{OC}_6\text{H}_4\text{CHO}$)

Carefully fractionated p-(allyloxy)benzaldehyde, a clear, water-white oil (yellowed on standing), exhibited the following constants: b.p. 120-121° at 5.0 mm. (reported: 142° at 10 mm. (21)); n_D^{25} 1.56646; d_4^{25} 1.08049; MR_D 48.996, calcd. 45.966; EM_D 3.030; EZ_D 1.868.

17. 4'-(Allyloxy)acetophenone ($p\text{-CH}_2=\text{CHCH}_2\text{OC}_6\text{H}_4\text{COCH}_3$)

Allyl bromide (67.8 g., 0.56 mole), 61.2 g. (0.45 mole) p-hydroxyacetophenone, 81.5 g. (0.59 mole) anhydrous potassium carbonate in 205 ml. acetone were refluxed nine hours. Acetone (135 ml.) was removed at atmospheric pressure to a maximum vapor temperature of 65°. After water was added, the oil layer which formed was separated

from the water layer, and the latter layer was extracted with ether; the oil and ether extracts were combined, washed with 5% aqueous sodium hydroxide, then water, and dried over anhydrous potassium carbonate. On fractionation of the crude product (75.2 g., 94.9%), 4'-(allyloxy)acetophenone (39.5 g., 49.9%) was obtained as a clear, water-white, viscous oil, m.p. 17.4° (reported: 20° (52)), b.p. $151-152^{\circ}$ at 11.0 mm. (reported: 137° at 7 mm. (52), $138-142^{\circ}$ at 10 mm. (92), $146-147^{\circ}$ at 10 mm. (1)), n_D^{25} 1.55267; d_4^{25} 1.06768; MR_D 52.808, calcd. 50.584; EM_D 2.224; EZ_D 1.262.

18. Allyl p-nitrophenyl ether ($p-O_2NC_6H_4OCH_2CH=CH_2$)

Allyl bromide (99.9 g., 0.825 mole), 104.3 g. (0.75 mole) p-nitrophenol, 104.0 g. (0.75 mole) anhydrous potassium carbonate in 150 ml. acetone were refluxed for eleven hours. After water was added and the mixture extracted with ether, the ether extracts were combined, washed with 5% aqueous sodium hydroxide, then water, and dried over anhydrous potassium carbonate. On fractionation of the crude product (122.6 g., 91.3%), allyl p-nitrophenyl ether (87.1 g., 64.8%) was obtained as a yellow oil (darkened rapidly on standing), m.p. 20.8° (reported: 18.5° (21), 36° (105)); b.p. $134.5-135.5^{\circ}$ at 4.0 mm. (reported: decomposition at 140° (105), 160° at 12 mm. (21)); n_D^{25} 1.57634;

d_4^{25} 1.19012; MR_D 49.847, calcd. 46.950 (118); EM_D 2.897;
 EZ_D 1.617.

E. Correlation of Exaltations with
Hammett's Sigma Values in Allyl
Phenyl Ethers

Physical constants and derived data for the allyl aromatic ethers described above are shown in Table 12, along with Hammett's sigma values for the ring substituents. Although the differences between EZ_D for allyl phenyl ether and the substituted allyl phenyl ethers are slight for sigma values from -0.268 through 0.391, a definite decrease in EZ_D is to be noted. Since phenyl propyl ether exhibits an exaltation somewhat larger than that for allyl phenyl ether, the contribution of the allyl double bond to the exaltation may be negligible. To clarify this point, the next section deals with the exaltations of anisole, phenetole, and cyclohexyl propyl ether, and the effect of ring substituents, especially the p-formyl, p-acetyl, and the p-nitro groups on the exaltation of anisole.

Figure 6 is a plot of the molecular and specific exaltations of the allyl aromatic ethers versus Hammett's sigma values for the ring substituents.

TABLE 12

PHYSICAL CONSTANTS AND DERIVED DATA FOR ALLYL AROMATIC ETHERS

Substituent	Boiling Point (°/mm.)	n_D^{25}	d_4^{25}	M_D	E_D	σ^-
p-OMe	113.0-113.5/9.5	1.52509	1.04258	0.675	0.411	-0.268
3,4-Me ₂	79.5-80.5/3.0	1.51951	0.96204	0.652	0.402	-0.229
p-t-Bu	109.0-109.5/6.5	1.50660	0.93460	0.739	0.388	-0.197
p-Me	72-73/4.8	1.51523	0.96133	0.553	0.374	-0.170
m-Me	80-81/7.0	1.51607	0.96188	0.589	0.398	-0.069
None	61.0/6.5	1.51935	0.97580	0.412	0.308	0.000
m-OMe	96.0/4.3	1.52618	1.04110	0.829	0.505	0.115
p-Cl	90-91/6.0	1.53468	1.12328	0.514	0.305	0.227
p-Br	98.5-99.0/4.7	1.55793	1.38499	0.494	0.232	0.232
m-Cl	87.0-87.5/6.0	1.53384	1.12195	0.506	0.300	0.373
m-Br	95-96/4.5	1.55716	1.38234	0.534	0.251	0.391
p-COCH ₃	151-152/11.0	1.55267	1.06768	2.224	1.262	0.874

TABLE 12 Continued

Substituent	Boiling Point (°/mm.)	n_D^{25}	d_4^{25}	EM_D	$E\sum D$	σ^-
p-CHO	120-121/5.0	1.56646	1.08049	3.030	1.868	1.126
p-NO ₂	134.5-135.5/4.0	1.57634	1.19012	2.897	1.617	1.27
o-Cl	92.5-93.0/6.5	1.53744	1.12322	0.714	0.423	-----
o-Me	75.0-75.5/7.0	1.51672	0.96476	0.501	0.338	-----
2,4-Cl ₂	106.5-107.5/4.8	1.55196	1.25502	0.628	0.310	-----
C ₆ H ₅ OPr	189/762	1.49863	0.94342	0.563	0.414	-----

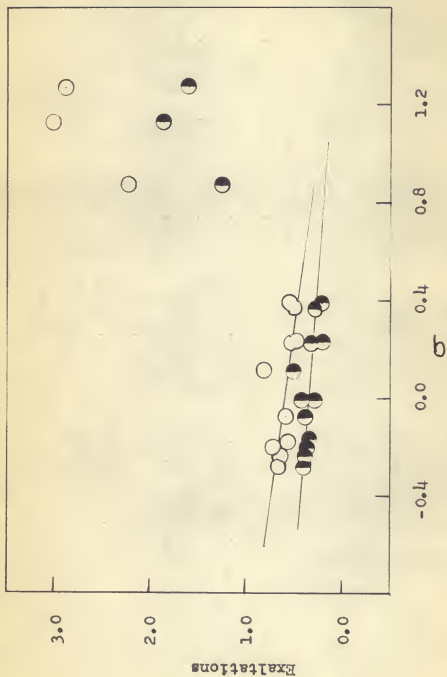


Fig. 6.--Variation of exaltations of allyl phenyl ethers with Hammett's sigma values for the substituents: ○, molecular exaltation; ◐, specific exaltation.

F. Exaltations of Alkyl Phenyl Ethers,
Phenyl Vinyl Ethers, Allyl Phenyl
Sulfide, and Phenyl Propyl Sulfide

The specific exaltations of anisole, phenetole, phenyl propyl ether, cyclohexyl propyl ether, phenyl propyl sulfide, and allyl phenyl sulfide are 0.354 (27, 84), 0.472 (27), 0.414 (27), 0.003 (125), 0.603 (50), and 0.506 (25, 46, 109), respectively; saturation of the ring in phenyl propyl ether removed the exaltation, while the other values may well be within the limits of experimental error.

The specific exaltations for several anisoles and phenyl vinyl ethers, together with the specific exaltations for several previously described allyl phenyl ethers, are shown in Table 13. The methyl substituents give rather similar increments in all three cases, while the exaltations for *p*-(allyloxy)benzaldehyde and allyl *p*-nitrophenyl ether are well above those found for *p*-methoxybenzaldehyde and *p*-nitroanisole. Data for 4'-(vinylloxy)acetophenone, *p*-(vinylloxy)benzaldehyde, and *p*-nitrophenyl vinyl ether were not available; one would expect their exaltations to be considerably enhanced over those for the corresponding allyl phenyl ethers.

TABLE 13
SPECIFIC EXALTATIONS FOR ANISOLES
AND PHENYL VINYL ETHERS

Substituent	C_6H_5OMe	$C_6H_5OCH=CH_2$	$C_6H_5OCH_2CH=CH_2$
p-Me	0.488(11)	0.752(100)	0.374
m-Me	0.452(4)	0.764(100)	0.398
None	0.354(27,84)	0.670(18,100)	0.308
p-COMe	1.275(3,26)	-----	1.262
p-CHO	1.20(3,26)	-----	1.868
p-NO ₂	1.27(11,26)	-----	1.617

CHAPTER VI

POLYMERIZATION STUDIES

Butler and Ingley (15) found that little work had been carried out on the polymerization of allyl phenyl ethers, and reported the boron trifluoride-catalyzed polymerization of several allyl phenyl ethers; they further noted that peroxide-induced polymerizations were unsuccessful. The apparent failure of peroxides to induce the polymerization of allyl phenyl ethers may be due to "degradative chain transfer" (8), resulting from an extremely reactive, non-resonance-stabilized radical. Since such radicals may yield chain transfer addition products (17, 64), one exploratory experiment was carried out involving the peroxide-catalyzed addition of bromotrichloromethane to allyl phenyl ether.

Although it was shown in Chapter II that there was little, if any, correlation of the exaltation of refraction with the rate of polymerization in homopolymerizations, the effect of free radical, cationic, and anionic catalysts on several allyl phenyl ethers was determined to serve as controls for subsequent copolymerization studies.

A. Materials

The various allyl phenyl ethers were described in previous chapters; sodamide, methanol, and acetone were from stock; allyl acetate was furnished by Dr. G. B. Butler, Department of Chemistry, University of Florida; the other chemicals were purchased: acrylonitrile and acrylamide (Matheson Coleman and Bell), benzoyl peroxide (Lucidol Division, Wallace and Tiernan, Incorporated), bromotrichloromethane (Dow Chemical Company), vinyl acetate (Eastman Kodak Company), ammonium persulfate (Merck and Company), boron trifluoride-etherate (Baker and Adamson), and sodium methylate (Columbia Organic Chemicals Company, Inc.).

B. Polymerization Procedure

Weighed amounts of reactants in 20-ml. ampoules were thoroughly swept with nitrogen, and the ampoules were cooled in Dry Ice-acetone before sealing off. Polymerizations were carried out in an oven held at 70°.

C. Homopolymerization of Allyl Phenyl Ethers

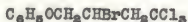
The boron trifluoride-catalyzed (1% by weight) polymerization of allyl phenyl ether at 70° proceeded rapidly and gave an apparently low molecular weight

product; the low molecular weight is to be expected since boron trifluoride-catalyzed polymerizations usually give polymers which decrease in molecular weight as the polymerization temperature is raised (111). Infrared spectra and refractive indexes showed allyl phenyl ether to be unchanged after treatment for 111 hours at 70° with 1% by weight of benzoyl peroxide, sodium methyrate, and sodamide. (Allylbenzene is readily isomerized to trans-propenylbenzene (79)).

Although data in Chapter V implied a negligible contribution of the allyl double bond to the exaltation in allyl phenyl ethers, the large exaltation of p-(allyloxy)-benzaldehyde suggested a possible polymerization by basic catalysts, and a slower polymerization by acid catalysts, due to the polarization in the aldehyde group. After 153 hours at 70° with 1% by weight of catalyst on the p-(allyloxy)-benzaldehyde, benzoyl peroxide produced no change, sodium methyrate gave indications of an extremely slow polymerization, while boron trifluoride gave a purple-red, mobile liquid rather than the low molecular weight polymer obtained in the case of allyl phenyl ether.

On the other end of the Hammett sigma scale, allyl p-tert-butylphenyl ether showed no change after 153 hours at 70° with 1% by weight of benzoyl peroxide.

D. Addition of Bromotrichloromethane
to Allyl Phenyl Ether



To explore the possibility of obtaining chain transfer addition products with allyl phenyl ethers, 99.6 g. (0.50 mole) bromotrichloromethane (b.p. 103° at 755 mm.), 13.4 g. (0.10 mole) allyl phenyl ether, and 4.8 g. (0.02 mole) benzoyl peroxide were heated slowly to 65° , at which temperature a vigorous reaction set in, and the temperature rose rapidly to 110° ; after an additional one hour at 100° and three hours at 70° , the reaction mixture was topped of bromotrichloromethane; fractionation of the crude product gave a light brown oil (25.5 g.; 76.5%, calculated as 2-bromo-4,4,4-trichlorobutyl phenyl ether); refractionation gave a clear, light yellow oil, b.p. $117-119^\circ$ at 1.7 mm., n_D^{25} 1.5627, d_4^{25} 1.526; MR_D 70.74, calcd. 68.79.

The apparent success of this reaction suggests similar preparations involving the peroxide-catalyzed addition of chloroform, bromoform, carbon tetrachloride, and carbon tetrabromide to allyl phenyl ethers to yield substituted phenyl 4,4,4-trichlorobutyl ethers, phenyl 2,4,4-tribromobutyl ethers, phenyl 2,4,4,4-tetrachlorobutyl ethers, and phenyl 2,4,4,4-tetrabromobutyl ethers. Searle (96) prepared phenyl 5,5,5-trichloroamyl ether

($C_6H_5OCH_2CH_2CH_2CH_2CCl_3$) via phenol and 1,1,1,5-tetrachloropentane. No references were found covering the peroxide-catalyzed addition of polyhalogenated compounds to allyl phenyl ether, although Kharasch (54-57) has reported on the peroxide-catalyzed addition of polyhalogenated compounds to olefins.

This one successful preparation further suggests the possible peroxide-catalyzed addition of chloroform, bromoform, bromotrichloromethane, carbon tetrachloride, and carbon tetrabromide to substituted phenyl vinyl ethers. The preparation of phenyl 1,1,2-tribromoethyl ether ($C_6H_5OCBr_2CH_2Br$) has been reported (76), but the synthesis did not involve a peroxide-catalyzed addition. The rather obvious resemblance of the compounds possessing terminal trichloromethyl groups to chloral hydrate (2,2,2-trichloro-1,1-ethanediol) and chlorobutanol ("Chloretone"; 1,1,1-trichloro-2-methyl-2-propanol) suggests possible pharmaceutical interest.

Additional reactions could involve the peroxide-catalyzed addition of a number of atoms and free radicals, and could include the addition of ethyl bromoacetate (57) to allyl phenyl ethers and phenyl vinyl ethers to yield substituted γ -bromo esters.

Now that a number of allyl phenyl ethers are available, their epoxidation with perbenzoic acid (127)

or their hydroxylation with potassium permanganate (65) or peroxytrifluoroacetic acid (30) might yield epoxypropanes or propanediols of potential interest.

E. Copolymerizations of Allyl Phenyl Ethers

1. Allyl phenyl ether and acrylonitrile

Acrylonitrile was dried over anhydrous potassium carbonate and was then fractionated; b.p. 77.0° at 753 mm. (reported: $77.2-77.4^{\circ}$ at 760 mm. (104)), n_D^{25} 1.3886 (reported: 1.3886 (104); 1.3889 (51)); d_4^{25} 0.80033.

Reaction of acrylonitrile and allyl phenyl ether at 70° for a maximum of eighteen hours in molar ratios of acrylonitrile to allyl phenyl ether from 0.1 to 1.0, and benzoyl peroxide from 0.1 to 1.0% by weight on the reactants gave only polyacrylonitrile.

2. Allyl phenyl ether and acrylamide

Reaction of acrylamide (0.025 mole) and allyl phenyl ether (0.025 mole) for a maximum of seventeen hours in methanol with 1.0% by weight of either benzoyl peroxide or ammonium persulfate gave only polyacrylamide. This result was expected, since acrylamide was reported (45) to polymerize at a faster rate than acrylonitrile.

3. Allyl phenyl ether and vinyl acetate

Vinyl acetate was fractionated; b.p. 72.6° at 760 mm. (reported: 72.4° (85)), $n_D^{25.5}$ 1.3910 (reported: n_D^{25} 1.3934 (85)).

Vinyl acetate polymerized quite rapidly in bulk and somewhat less rapidly in benzene (107) at 70° with 0.5% by weight benzoyl peroxide. However, equimolar amounts of vinyl acetate and allyl phenyl ether in bulk, benzene solution, and acetone solution, with 0.5% by weight of either ammonium persulfate or benzoyl peroxide on the reactants resulted in no change in the reactants, and complete inhibition of the polymerization of the vinyl acetate. Bulk copolymerizations of equimolar amounts of allyl phenyl ether and vinyl acetate with up to 3.0% by weight of benzoyl peroxide on the reactants resulted in the recovery of the monomers.

4. Allyl phenyl ether and allyl acetate

Allyl acetate was washed twice with cold, saturated aqueous sodium acid carbonate, twice with cold, saturated aqueous calcium chloride, dried over anhydrous potassium carbonate, and fractionated; b.p. 102.5 - 103.5° at 762 mm. (reported: 102.3 - 103.2° (80)), $n_D^{25.5}$ 1.4002 (reported: n_D^{18} 1.4046 (80), n_D^{25} 1.4009 (82)).

Allyl acetate polymerized rather slowly at 70° with 6.0% by weight of benzoyl peroxide. Allyl phenyl ether showed no change at 70° with 6.0% by weight of benzoyl peroxide. Copolymerization of allyl phenyl ether (0.025 mole) and allyl acetate (0.025 mole) at 70° for 187 hours with 6.0% by weight of benzoyl peroxide on the reactants showed no polymerization of the allyl phenyl ether and negligible polymerization of the allyl acetate.

5. Allyl p-tert-butylphenyl ether and p-(allyloxy)benzaldehyde

Allyl phenyl ethers containing ring substituents at opposite ends of the Hammett sigma scale offered the most hope for free radical-catalyzed copolymerization (91). However, allyl p-tert-butyl phenyl ether (0.017 mole), p-(allyloxy)benzaldehyde (0.017 mole), and benzoyl peroxide (0.00025 mole) showed no change after 153 hours at 70°.

CHAPTER VII

SUMMARY

Recognizing that nuclear and side-chain substituents either increase, retard, or inhibit polymerizations, it was decided to investigate a possible correlation between the exaltation of refraction of several allyl phenyl ethers and their rates of polymerization.

Preliminary to the actual work on the allyl phenyl ethers, evaluation of the literature on a number of substituted styrenes showed that it was not possible to correlate exaltations with reactivity rates in homopolymerizations. However, in both free radical and ionic copolymerizations involving similar monomers, plots of the logarithms of the relative reactivities of several substituted styrenes toward the styrene and methyl methacrylate radicals versus the differences existing between the exaltations of substituted styrenes and the exaltation of styrene were strikingly similar to those in which Hammett's sigma values for the styrene substituents were plotted against the relative reactivities of the substituted styrenes. In the free radical copolymerization of α -methylstyrenes with maleic anhydride, the relative

reactivities of the α -methylstyrenes toward the maleic anhydride radical showed little relation to the differences existing in the exaltations of the α -methylstyrenes and α -methylstyrene; similarly, these relative reactivities showed little relation to the Hammett sigma values for the α -methylstyrene substituents.

With the exception of allyl phenyl ether and allyl o-chlorophenyl ether, density and refractive index data were not available for the calculation of the exaltations of refraction for the seventeen allyl phenyl ethers described in this work. The required ethers were prepared by the reaction of allyl bromide with a substituted phenol in acetone in the presence of either anhydrous potassium carbonate or aqueous sodium hydroxide; physical measurements were made on the freshly distilled ethers.

The exaltations for the allyl phenyl ethers were almost identical for Hammett sigma values from -0.268 (p-methoxy) through 0.391 (m-bromo), with a slight, but probably significant, decrease in exaltation in this sigma range. Since phenyl propyl ether exhibited an exaltation somewhat larger than that for allyl phenyl ether, the contribution of the allyl double bond to the exaltation was negligible; saturation of the ring in phenyl propyl ether removed the exaltation. The exaltation of allyl phenyl ether was considerably enhanced by

the introduction of *p*-formyl, *p*-acetyl, and *p*-nitro groups; a parallel but somewhat less pronounced enhancement was found in similarly-substituted anisoles.

Peroxides failed to induce polymerization of the allyl phenyl ethers, possibly due to the formation of extremely reactive, non-resonance-stabilized radicals. Since such radicals may yield chain transfer addition products, one exploratory experiment was carried out in which bromotrichloromethane added vigorously to allyl phenyl ether in the presence of benzoyl peroxide. The success of this reaction suggests the addition of atoms, radicals, and other polyhalogenated compounds to allyl phenyl ethers and phenyl vinyl ethers. The attempted peroxide-catalyzed copolymerization of allyl phenyl ether with acrylamide and acrylonitrile gave only polyacrylamide and polyacrylonitrile, respectively. Allyl phenyl ether completely inhibited the peroxide-catalyzed polymerization of vinyl acetate.

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BIOGRAPHICAL ITEMS

Paul M. Downey was born April 28, 1915, in Nashua, New Hampshire. After attending the public schools of Nashua, he entered the Worcester Polytechnic Institute, Worcester, Massachusetts, in 1932, and received the Bachelor of Science degree in 1936. He entered the Graduate School of the University of New Hampshire in 1936, and received the Master of Science degree in 1938.

He was then employed by the Monsanto Chemical Company, Nitro, West Virginia, as a research chemist until June, 1942, when he entered the United States Army Air Corps as an Aviation Cadet. After discharge from the Air Corps as a Major in November, 1945, he returned to the Monsanto Chemical Company as a research chemist, and was appointed a Group Leader in 1949, and Coordinator of Rubber Chemical Research in 1951.

He entered the Graduate School of the University of Florida in February, 1953, where he served as a Teaching Assistant until August, 1955, as the du Pont Teaching Fellow to June, 1956, and as a Teaching Assistant during the Summer Session of 1956.

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